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MRL-TN-393

AR-000-294

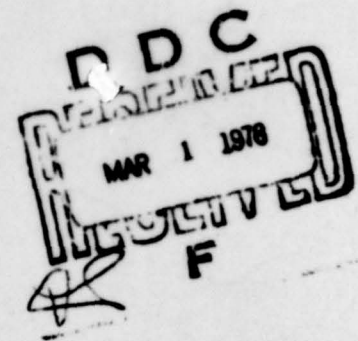


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TECHNICAL NOTE

MRL-TN-393



THE DETERMINATION OF SODIUM CRYOLITE IN PROPELLANTS
VIA THE ALUMINIUM CONTENT

R. G. Davidson and F. D. McPherson

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FEBRUARY 1977

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SUMMARY

The determination of the sodium cryolite (Na_3AlF_6) content in propellant via the aluminium content has been investigated. Two methods for the determination of aluminium were examined and the results were compared with those obtained from the determination of sodium cryolite via its fluorine content by the standard distillation method. The two methods for the determination of aluminium were complexometric titration, and spectrophotometry with 8-hydroxyquinoline. The results show that sodium cryolite in propellant may be determined more rapidly and more easily via the aluminium content than via the fluorine content.

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POSTAL ADDRESS: Chief Superintendent, Materials Research Laboratories,
P.O. Box 50, Ascot Vale, Victoria 3032, Australia

DOCUMENT CONTROL DATA SHEET

Security classification of this page:

UNCLASSIFIED

1. DOCUMENT NUMBERS:

a. AR Number AR-000-294

b. Series & Number:

TECHNICAL NOTE MRL-TN-393

c. Report Number 14 MRL-TN-393

2. SECURITY CLASSIFICATION:

a. Complete document:

UNCLASSIFIED

b. Title in isolation:

UNCLASSIFIED

c. Summary in isolation:

UNCLASSIFIED

3. TITLE:

6 THE DETERMINATION OF SODIUM CRYOLITE IN PROPELLANTS
VIA THE ALUMINIUM CONTENT.

4. PERSONAL AUTHOR(S):

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F.D. McPHERSON

5. DOCUMENT DATE:

11 FEB 1977

6. TYPE OF REPORT & PERIOD COVERED:

9 Technical note.

7. CORPORATE AUTHOR(S):

Materials Research Laboratories

8. REFERENCE NUMBERS:

a. Task: DEF 99/016(b)

b. Sponsoring Agency:

9. COST CODE: 331590

10. IMPRINT (Publishing establishment)

Materials Research Laboratories,
P.O. Box 50, Ascot Vale, Vic. 3032
FEBRUARY, 1977

11. COMPUTER PROGRAM(S):

(Title(s) and language(s)):

12 12 p.

12. RELEASE LIMITATIONS (of the document):

Approved for public release

12-0. OVERSEAS: ☐ N.O. ☐ P.R. ☒ 1 ☐ A ☐ B ☐ C ☐ D ☐ E ☐

13. ANNOUNCEMENT LIMITATIONS (of the information on this page):

No limitation

14. DESCRIPTORS:

Propellants; Chemical Analysis; Cryolite

15. COSATI CODES: 1901, 2109, 0704

16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

The determination of the sodium cryolite (Na_3AlF_6) in propellant via the aluminium content has been investigated. The results obtained are comparable with those obtained by the standard distillation method for the determination of fluorine. Determination of the aluminium content is quicker than the standard distillation method and requires less skill.

A	ACCESS	BY	DATE
	NTS	BY	DATE
	DOC	BY	DATE
	UNCLASSIFIED	BY	DATE
JUSTIFICATION		SPECIAL	

409014

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THE DETERMINATION OF SODIUM CRYOLITE IN PROPELLANTS
VIA THE ALUMINIUM CONTENT

1. INTRODUCTION

The method currently used at these laboratories for the determination of sodium cryolite in propellants is the standard distillation procedure described in D.O.T.M. 4286, 5.A.(1) (1). In that method, the propellant is gelatinised with an ether/alcohol mixture and liquid paraffin in the presence of magnesium acetate as a carrier, and then ignited. The resultant ash is dispersed in 65% w/w sulphuric acid, silica is added and the fluoride is steam distilled as fluosilicic acid. The fluoride in the distillate is determined by titration with thorium nitrate solution in the presence of Alizarin Red S indicator. Gollop (2) reported that the method has several disadvantages:-

- (i) It is a lengthy procedure that requires close operator attention throughout, and there are several points during the analysis at which mechanical losses may occur.
- (ii) Finely divided carbon, from incomplete ignition, and foreign salts, can cause interference during the volatilisation of the fluosilicic acid.
- (iii) The end point of the titration is rather subjective and requires experience in its detection.

Although the grade of sodium cryolite used in propellant manufacture is not of high purity the stoichiometry is close enough to theoretical to allow the determination of either sodium or aluminium to be used as a measure of the sodium cryolite content of the propellant (Table 3). Sodium may be determined by atomic absorption spectrophotometry, or flame photometry, as well as by the traditional precipitation as sodium magnesium uranyl acetate. However, the common distribution of sodium salts in the environment could lead to significant contamination of the propellant during manufacture and perhaps in the analysis. There is less likelihood of contamination by aluminium salts, so that element was considered to be more suitable than sodium as a measure of the sodium cryolite content of propellants.

Macorkindale (3) has described the use of perchloric acid for the rapid and controlled decomposition of propellants. That method was used to replace the lengthy gelatinisation and ignition procedure. Two methods for the determination of aluminium were examined:-

- (i) Complexometry by back titration of excess disodium ethylenediaminetetra acetic acid (EDTA) with Cu^{II} in the presence of 1,(2-pyridylazo)-2-naphthol (PAN) indicator at pH \sim 5.
- (ii) Measurement of the absorbance of the aluminium/8-hydroxyquinoline (oxine) complex, after extraction into chloroform from an aqueous solution at pH \sim 10.

Three samples of propellant were analysed by the two methods, and the results compared with each other and with those obtained from the analysis of the same propellants by the standard distillation procedure (Table 1). The time required for each method was also recorded (Table 5).

The repeatability of each method was determined from the results of ten replicate analyses of the same sample by each method (Table 2 and Table 4). The results of these analyses were also used for a statistical comparison of the three methods, (Student's "t" test; "F" test).

The object of the work reported in this note was to establish the feasibility of the determination of sodium cryolite in propellant via the aluminium content rather than the fluoride content, in order to both shorten the analysis time, and to eliminate the problems reported by Gollop (2). It is not intended that the procedures described here should be regarded as standard methods. Indeed, for routine work involving large numbers of samples, it is probable that atomic absorption spectrophotometry would be the most economical method.

2. EXPERIMENTAL

2.1 Apparatus

Zeiss PMQII single beam spectrophotometer.

2.2 Materials

2.2.1 Reagents

All chemicals and solvents were analytical reagent grade, used as received, except sodium cryolite which was propellant grade material (98% minimum, Al + Na + F).

2.2.2 Propellants

The propellants used were NQ/M .018, NQ/M .028 and NQ/M .054 of the nominal composition:

Picrite (1-nitro-guanidine)	55.0%
Nitrocellulose	20.8%
Nitroglycerine	20.6%
Ethyl centralite*	3.6%
Sodium cryolite (added)	0.3%

*1,3-diethyl-1,3-diphenyl urea.

2.3 Methods

2.3.1 Determination of Aluminium by Complexometric Titration

The sample of propellant (2 g) was decomposed by heating it gently with 55-60% m/v perchloric acid (20 cm³) (Note 1) in a 250 cm³ conical flask with a small funnel in the neck of the flask to minimise mechanical losses. Heating was discontinued when the reaction started and the exothermal decomposition allowed to proceed. When the reaction had subsided the solution was heated (to fumes of perchloric acid), cooled, the funnel and neck of the flask rinsed down with water and the solution reheated (to fumes of perchloric acid) to complete the destruction of the organic matter and removal of fluoride (Note 2).

The solution was then diluted to approximately 100 cm³ with distilled water, boiled to eliminate chlorine and an excess of 0.01 M EDTA (20.0 cm³) added. The solution was neutralised to methyl red with 25% m/v sodium hydroxide and buffered with sodium acetate (3 g) and glacial acetic acid (1 cm³). The solution was boiled for two minutes, cooled to 80°C and the excess EDTA titrated with 0.01 M copper^{II} nitrate solution using 1,(2-pyridylazo)-2 Naphthol (PAN) indicator (0.1% m/v in ethanol). The colour change is from yellow/green to violet. The solutions should be standardised against pure aluminium.

NOTE 1

The concentration of the perchloric acid is critical, greater than 60% m/v causes a violent reaction and may result in fire or explosion, much less than 55% m/v gives a very slow reaction (3).

NOTE 2

As aluminium forms a stronger complex with fluoride than with EDTA the rinsing down and reheating is necessary to remove all traces of fluoride. If the solution, on cooling, is any darker than a pale straw colour the solution should be diluted with water and be heated again (to fumes of perchloric acid).

2.3.2 Spectrophotometric Determination of Aluminium with Oxine

The sample of propellant (2 g) was decomposed as in 2.3.1 and the solution diluted to 250 cm³ in a volumetric flask. 50.0 cm³ was transferred to a 250 cm³ separating funnel, neutralised to litmus with ammonia (d = 0.880) and 1 cm³ of buffer solution added (54 g of ammonium chloride and 300 cm³ of ammonium hydroxide diluted to 1000 cm³ with distilled water). Oxine (1% m/v in chloroform, 10.0 cm³) was added, the funnel stoppered and shaken. The layers were allowed to separate and the organic layer transferred to a 100 cm³ volumetric flask. This step was repeated once, then the aqueous layer was washed three times with chloroform (20 cm³) and the washings collected in the volumetric flask. The solution was diluted to the mark with chloroform, and anhydrous sodium sulphate (2 g) added to remove any entrained water. The absorbance was measured at 392 nm in 0.5 cm cells with a reagent blank as the reference. A calibration curve was prepared from pure aluminium dissolved in dilute hydrochloric acid.

2.3.3 Standard Distillation Procedure: (D.O.T.M. 4286) (1)

The sample was gelatinised with ether/alcohol, diluted with paraffin oil and ignited. The residue was transferred to a distillation flask with 65% sulphuric acid and a small amount of silica added. Fluosilicic acid was steam distilled from the mixture at 135°C and the fluorine in the distillate was titrated with thorium nitrate solution to Alizarin Red S indicator. The thorium nitrate was standardised against pure sodium fluoride, and the theoretical figure (54.3%) for fluorine in sodium cryolite was used to calculate the sodium cryolite content of the propellant.

3. RESULTS AND DISCUSSION

3.1 Determination of Aluminium by Complexometric Titration

The decomposition of propellant samples with perchloric acid is a rapid and controllable method for destruction of organic matter (3), provided that the mouth of the flask is closed with a small funnel to prevent possible losses by splashing, and the strength of the acid is kept at 55-60% m/v to prevent a too vigorous initial reaction. However, because of the hazards involved in the use of perchloric acid, strict safety precautions (e.g. the use of an efficient fume cupboard, wearing of eye protection and the freedom of the working area from any easily oxidisable material) should be observed.

The end point colour change, under the conditions described, is very sharp and is easy to detect by an inexperienced operator.

3.2 Spectrophotometric Determination of Aluminium with Oxine

As the method of sample decomposition is the same as that used in 2.3.1 the comments made in 3.1 are valid for this method.

The use of a spectrophotometer to measure absorbance replaces the visual assessment of a colour change (as in the titrations) and this eliminates any possible personal prejudice regarding the end point. However

a calibration curve must be prepared for each series of analyses, which adds to the work load and the time involved.

3.3 Standard Distillation Method

There are several points during this analysis where mechanical losses can occur:

- (i) While gelatinising the sample, because of splashing and sample adhering to the stirrer.
- (ii) During ignition if the gelatinisation is not complete and the ignition is too vigorous.
- (iii) While transferring the residue to the distillation flask and by spitting when the sulphuric acid is added.

Care must be taken during ignition to remove as much of the carbonaceous matter as possible. Gollop (2) reported that finely divided carbon and foreign salts caused interference in the volatilisation of the fluosilicic acid and the 15 minutes ignition time recommended in the method may not be long enough. In addition, the temperature is not specified.

During the distillation external heating and steam flow must be carefully balanced to maintain the optimum temperature of 135°C.

The end point of the thorium nitrate titration is not a sharp colour change in the solution but a subtle colour change on the precipitate. An experienced analyst is required and the end point is quite subjective.

3.4 Analysis of Sodium Cryolite

Analysis of propellant grade sodium cryolite by the specification methods for that material (4) gave the results shown in Table 3. The material does not meet the specification requirements, but it appears to be a typical representative of propellant grade sodium cryolite.

3.5 Comparison of the Results from the Three Methods

At first sight, (Table 2) it would appear that there are statistically significant differences between any pair of the three methods, though for practical purposes there is no significant difference between any of the results because the propellant specification limits are quite wide at $0.3\% \pm 0.1\%$. However, the repeatability of the complexometric titration method is significantly better than either of the other two methods.

In 3.4 above, and Table 3 it was shown that the sodium cryolite incorporated into propellant does not contain the theoretical amounts of either fluorine or aluminium, the former is lower than theoretical, and the latter is higher. Since the sodium cryolite content of propellant is calculated on the basis of theoretical factors irrespective of the method of analysis, then a direct comparison of the results obtained via analyses for two different elements is not reasonable. It can be seen that the sodium cryolite content of propellants calculated from the fluoride content is too

low by a factor of $54.3/52.4 = 1.04$ and that calculated from the aluminium content is too high by a factor of $13.1/12.85 = 1.02$. When the results given by the various methods are corrected by these factors, the differences between the methods become much less, and in fact there is now no significant difference between the distillation method and the complexometric titration (Table 4). The spectrophotometric method is seen to give significantly lower results than the complexometric titration and is just within the limit of significance when compared with the distillation method. Comparison of the variances of the three methods ("F" test) showed that both the distillation method and the spectrophotometric method are significantly more variable than the complexometric titration method, but do not differ significantly from each other.

3.6 Time Required for Analysis

Table 5 shows that the complexometric method is much quicker than the other two. For a single sample, the time required for the spectrophotometric method is similar to that required for the distillation method, but multiples of samples can be handled in a shorter time by the former method than the latter.

4. CONCLUSIONS

- (i) The sodium cryolite content of propellants can be determined more conveniently via the aluminium content than via the fluoride content without loss of either accuracy or precision.
- (ii) Complexometric titration is preferred for the determination over the spectrophotometric method because of its superior precision, shorter working time and simpler operation.

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T A B L E 1

DETERMINATION OF THE SODIUM CRYOLITE CONTENT
OF PROPELLANT BY 3 METHODS

Sodium Cryolite, %

Sample	Fluorine Distillation	Complexometric Titration	Spectrophotometrically with Oxine
1	0.32, 0.35	0.34, 0.34	0.32, 0.34
2	0.35, 0.35	0.37, 0.37	0.36, 0.35
3	0.36, 0.37	0.38, 0.38	0.36, 0.37

T A B L E 2

COMPARISON OF THREE METHODS FOR THE DETERMINATION
OF SODIUM CRYOLITE IN PROPELLANT

	Fluorine Distillation	Complexometric Titration	Spectrophotometrically with Oxine
Mean, %	0.33	0.36	0.35
Range	0.32 - 0.35	0.35 - 0.36	0.33 - 0.36
Standard Deviation, s	0.0090	0.0030	0.0090

For N = 10 t = 2.26

± 2.3s 0.021 0.007 0.021

Tests for significant differences between methods:

Distillation vs complexometry, t = 9.2

Distillation vs spectrophotometry t = 3.2

Spectrophotometry vs complexometry t = 4.1

for n = 18, t = 2.1 for P = 0.05 (i.e. 95% confidence level).

T A B L E 3

ANALYSIS OF SODIUM CRYOLITE BY PROCEDURES DESCRIBED IN
U.K. CHEMICAL INSPECTORATE LABORATORY METHOD M874/68

Element	Found	Theory, for Na_3AlF_6	Specification CS5114A
Sodium, %	30.5	32.95	} 98.0% min
Aluminium, %	13.1	12.85	
Fluorine, %	52.4	54.2	
Total, %	96.0	100.00	98.0% min

T A B L E 4

COMPARISON OF THREE METHODS FOR DETERMINATION OF SODIUM
CRYOLITE IN PROPELLANT. RESULTS CORRECTED FOR
DEVIATIONS FROM THEORETICAL ALUMINIUM AND
FLUORINE IN SODIUM CRYOLITE.

Method	Complexometry	Distillation	Spectrophotometry
Mean, %	0.352	0.347	0.339
Variance	7.6×10^{-6}	7.3×10^{-5}	8.7×10^{-5}

Statistical tests: $N_1 = N_2 = N_3 = 10$

	t	F
Distillation vs complexometry	1.44	9.6
Distillation vs spectrophotometry	2.05	1.2
Complexometry vs spectrophotometry	4.01	11.4

For $n = 18$, $t = 2.1$ for $P = 0.05$ (95% confidence level)

For $v_1 = v_2 = 9$, $F = 3.2$ (95% confidence level)

TABLE 5

TIME REQUIRED FOR THE DETERMINATION OF SODIUM CRYOLITE
IN PROPELLANTS BY THREE DIFFERENT METHODS

	Fluorine Distillation	Complexometric Titration	Spectrophotometry
Working Time, hours			
1 Sample	2.5	1.25	2.75
2 Samples	3.0	1.50	3.0
Elapsed Time, hours			
1 Sample	3.25	1.50	3.0
2 Samples	4.75	1.50	3.25

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